deny rational progress towards the solution of the innumerable and weighty problems confronting us.

Let me say in conclusion that it is my firm belief that in the untrammeled concentrated study of the phenomena of disease, with the ward as the laboratory, will medicine become truly scientific (in the best sense of that word), therefore truly rational, with hopes of conquest its best endeavor and success its ultimate goal. The change will evolve a man better taught, better trained and possibly possessed of better judgment. The numbers of those who practise or pursue the "art" of medicine will yet increase and reap larger and more abundant rewards in satisfaction of work well done than has hitherto been dreamed of. For the new era will demand the survival of the fittest to survive, and the practise of the profession of medicine will in even greater degree be counted the most honorable of all professions.

<div align="right">NORMAN MACL. HARRIS</div>

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THEORIES OF SOLUTIONS[1]

TWENTY-ONE years ago the Chemistry Section of the British Association at its meeting in Leeds was the scene of a great discussion on the nature of solutions. It was my first experience of a British Association meeting, and I well remember the stimulating effect of the lively discussion on all who took part in it. To-day, speaking from the honorable position of president of the section, I conceive I can do no better than indicate the position of the question at the present time. And this appears to me the more appropriate as our science has had this year to mourn the departure of van't Hoff, the founder of the

[1] Address of the president of the Chemical Section of the British Association for the Advancement of Science. Portsmouth, 1911.

modern theory of solution, whose name will remain one of the greatest in theoretical chemistry—in time to come, it will, I think, be considered almost the greatest. He had expressed the hope that he might attend this meeting as he did that twenty-one years ago. The hope is not fulfilled: his activity is merged in the final equilibrium of death. But his ideas are part and parcel of the chemical equipment of every one of us, and we know that whatever form the fundamental conceptions of chemistry may assume, the quantitative idea of osmotic pressure will be to the theory of solution what the quantitative idea of the atom is to chemical composition and properties. For I must emphasize the fact that chemistry is essentially a quantitative science, and no chemical theory, no partial chemical theory even, can be successful unless its character is quantitative. To quote the words of Lord Kelvin:

> I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you can not measure it, when you can not express it in numbers, your knowledge is of a meager and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely in your thoughts advanced to the stage of science.

A general theory of solutions must be applicable to all solutions—to those in which solvent and solute exist in practically mere intermixture, as well to those in which solute and solvent are bound together in what we can not sharply distinguish from ordinary chemical union. Between these extremes all grades of binding between solvent and solute exist, and it may be well to give a few examples illustrating the various types of solution.

Where no affinity exists between solvent and solute, the solution is practically of the same type as a mixture of two gases which are without chemical action on each other. The solute is merely diluted by the solvent

and retains its properties unchanged. An example of this type of solution may be found in the solution of one saturated hydrocarbon in another, say of pentane in hexane. On mixing the two liquids there is no evidence of union between them, the volume of the mixture is practically the sum of the volume of the components, the heat of solution is practically *nil*, the vapor pressure of each constituent is reduced merely as if by dilution with the other constituent, and so on. That there is some action between the two components even in this extreme case must be admitted, but it may be referred entirely to action of a physical kind, such as one finds on mixing one gas with another at considerable pressures. Action of a chemical nature is absent. If it be said that even saturated hydrocarbons have some chemical affinity for each other, recourse may still be had for examples to mixtures of two inactive elements, say liquid argon and liquid krypton, where chemical affinity is non-existent.

At the other extreme we have such solutions as those of sulphuric acid and water. Here there is every physical evidence of chemical union. The volume of the mixture is by no means the sum of the volumes of the components, the amount of heat evolved on mixing is very great, the separate liquids, which are practically non-conductors, yield on mixing a solution which is a good conductor, and so on. There is obviously here a great influence of the solvent water on the solute sulphuric acid, and this influence we can only account for by assuming that it is essentially chemical in character.

As the influence in such a case is necessarily reciprocal, then if even one of the constituents of the solution is inactive chemically there can plainly be no action of a chemical nature on mixing. Thus, no matter what solvent we take, it can exercise no action other than that of a physical kind on argon, say, which has been dissolved in it; and, again, if liquid argon is chosen as solvent no substance dissolved in it can be affected by it chemically, and we thus obtain only the properties of a physical mixture. It is convenient therefore to classify liquid solvents according to their chemical activity. The saturated hydrocarbons, which are chemically very inert, and, as their name paraffin implies, little disposed to chemical action of any kind, may be taken as typically inactive solvents, analogous to liquid argon. Water, on the other hand, as its numerous compounds (hydrates) with all kinds of substances testify, may be taken as a typically active solvent. The ordinary organic solvents exhibit intermediate degrees of activity.

For the purpose of illustrating the effect of solvents on a dissolved substance one may conveniently take a colored substance in a series of colorless solvents. If the substance is unaffected by the solvent, we might reasonably expect the color of the solution to be the same as the color of the vapor of the substance at equal concentration. Iodine, for instance, gives rise to the familiar violet vapor. Its solution in carbon disulphide has a color practically similar, but its solution in alcohol or water is of a brown tint quite different from the other. In the indifferent hydrocarbons and in chloroform the color is like that in carbon disulphide, in methyl or ethyl alcohol it is brown. We conclude therefore roughly that iodine dissolved in saturated hydrocarbons, in chloroform, carbon tetrachloride and carbon disulphide is little affected by the solvent, whereas in water and the alcohols it is greatly affected, probably by way of combination, since in all the solvents two atoms of iodine seem to be associated in the molecule. That combination between the iodine and the active solvents has really

occurred receives confirmation from the behavior of iodine in dilute solution in glacial acetic acid. If the color of this solution is observed in the cold it is seen to be brown, resembling in color the aqueous solution. If the solution be now heated to the boiling-point, the color changes to pink, which may be taken to indicate that the compound of iodine and acetic acid which is stable at the ordinary temperature becomes to a large extent dissociated at 100°.

Now, as I have said, a general theory of solution must be applicable to all classes of solution, and herein lies the importance of van't Hoff's osmotic pressure theory. It applies equally to mixtures of gases, to mixtures of inert liquids, and to mixtures such as those of sulphuric acid and water; and it has the further advantage that so long as the solutions considered are dilute there are simple relations connecting the osmotic pressure with other easily measurable properties of the solutions. It has been unfortunately the custom to oppose the osmotic pressure theory of solution to the hydrate, or more generally the solvate, theory, in which combination between solute and solvent is assumed. The solvate theory is, in the first place, not a general theory, and in the second place it is perfectly compatible with the osmotic pressure theory. It is in fact with regard to a general theory of solutions on the same plane as the electrolytic dissociation theory of Arrhenius. This theory of ionization applies to a certain class of solutions, those, namely, which conduct electricity, and is a welcome and necessary adjunct in accounting for the numerical values of the osmotic pressure found in such solutions. Similarly the hydrate, or more generally the solvate, theory is applicable only to those solutions in which combination between solvent and solute occurs, and will no doubt in time afford valuable information with regard to

the osmotic pressure, especially of concentrated solutions in which the affinity between solvent and solute is most evident. It can tell us nothing about solutions in which one, or both, components is inactive, just as the electrolytic dissociation theory can tell us nothing about solutions which do not conduct electricity.

The great practical advantage bequeathed to chemists by the genius of van't Hoff is the assimilation of substances in dilute solution to substances in the gaseous state. Here all substances obey the same physical laws, and a secure basis is offered for calculation connecting measurable physical magnitudes, irrespective of the chemical nature of the substances and of the solvents in which they are dissolved, provided only that the solutions are non-electrolytes. If the solutions are electrolytes, the dissociation theory of Arrhenius, developed independently of the osmotic pressure theory of van't Hoff, gives the necessary complement, and for aqueous solutions offers a simple basis for calculation. Van't Hoff has given to science the numerically definable conception of osmotic pressure; Arrhenius has contributed the numerically definable conception of coefficient of activity of electrolytes in aqueous solution, or what is now called the degree of ionization.

Of late there has been a tendency in some thermodynamical quarters to belittle the importance of the conception of osmotic pressure. It is quite true that from the mathematical thermodynamical point of view it may be relegated to a second place, and even dispensed with altogether, for it is thermodynamically related to other magnitudes which can be substituted for it. But it may be questioned if without the conception the cultivators of the thermodynamic method would ever have arrived at the results obtained by van't Hoff through osmotic pressure. Van't Hoff was

only an amateur of thermodynamics, but the results achieved by him in that field are of lasting importance, and his work and the conception of osmotic pressure have given a great stimulus to the cultivation of thermodynamics to chemistry.

And here we trench on a question on which a certain confusion of thought often exists. To the investigator it is open to choose that one of several equivalent methods or conceptions which best suits his personal idiosyncrasy. To the teacher such a choice is not open. He must choose the method or conception which is most clearly intelligible to students, and is at the same time least likely to lead to misconception. Osmotic pressure is a conception which the chemical student of mediocre mathematical attainments can grasp, and it is not difficult to teach the general elementary theory of dilute solutions by means of it and of reversible cycles without liability to radical error or misconception. I should be sorry on the other hand to try to teach the theory of solutions to ordinary chemical students by means of any thermodynamic function. The two methods are thermodynamically equivalent, and the second is mathematically more elegant and in a way simpler, but it affords less opportunity than the first for the student to submit his methods to any practical check or test, and in nine cases out of ten would lead to error and confusion. The difficulty of the student is not the mathematical one; with the excellent teaching of mathematics now afforded to students of physics and chemistry the mathematical difficulty has practically disappeared—the difficulty lies in critically scrutinizing the conditions under which each equation used is applicable.

Of the mechanism of osmotic pressure we still know nothing, but with the practical measurement of osmotic pressure great advances have been made in recent years.

In particular the admirable work of Morse and Frazer is of the first importance in establishing for solutions up to normal concentration the relationship between osmotic pressure and composition, and its variation with the temperature. Much may be anticipated from the continuation of these accurate and valuable researches, the experimental difficulties of which are enormous.

We are indebted to America not only for these researches, and for the voluminous material of H. C. Jones and his collaborators dealing with hydrates in solution, but also to A. A. Noyes and his school for accurate experimental work and for systematic treatment of solutions on the theoretical side. They, and also van Laar, have shown how solutions not coming within the ordinary range of dilute solutions to which van't Hoff's simple law is applicable, may in some cases at least be made amenable to mathematical treatment. Van't Hoff chose one simplification of the general theory by considering only very dilute solutions, for which very simple laws hold good, just as they do for dilute gases. Even a single gas in the concentrated or compressed form diverges widely from the simple gas laws; much more then may concentrated solutions diverge from the simple osmotic pressure law. The other simplification is to consider solutions of which the components are miscible in all proportions and are without action on each other; and this method has been developed with marked success from the point of view of osmotic pressure and other colligative properties.

The outstanding practical problem in the domain of electrolytic solutions is to show why the strong electrolytes are not subservient to the same laws as govern weak electrolytes. If we apply the general mass-action law of chemistry to the electrically active and inactive parts of a dissolved substance

(the ions and un-ionized molecules) as deduced from the conductivities by the rule of Arrhenius, we find that for a binary substance a certain formula connecting concentration and ionization should be followed, a formula which we know by the name of Ostwald's dilution law. This law seems to be strictly applicable to solutions of feeble electrolytes, but to solutions of strong electrolytes it is altogether without application. Wherein lies the fundamental difference between these two classes of solutions? Two kinds of explanation may be put forward. First, the ionized proportion may not be given accurately for strong electrolytes by the rule of Arrhenius; or second, the strong electrolytes do not obey the otherwise general law of active mass, which states that the activity of a substance is proportional to its concentration. The first mode of explanation has been practically abandoned, for other methods of determining ionization give values for strong electrolytes in sufficient agreement with the values obtained by the method of Arrhenius. The other explanation is that for some reason the law of active mass is, apparently or in reality, not obeyed by some or all of the substances in a solution of a strong electrolyte. An apparent disobedience to the law of mass-action would, for example, be caused by the formation of complexes such as Na_2Cl_2, or Na_2Cl^+ or $NaCl_2^-$ in a solution of sodium chloride. Mere hydration, e. g., the formation of a complex $NaCl_1 \, 2 \, H_2O$, would not affect the mass-action law in dilute solution, and the electrolyte would obey the dilution law in solutions of the concentration usually considered. A somewhat similar explanation, which takes into account the properties of the solvent, is that the ionizing power of the solvent water undergoes a noticeable change when the concentration of the ions in it increases beyond a certain limit.

I should wish now to draw attention to a point of view which has not, so far as I am aware, been fully considered. To begin with we may put to ourselves the question: Is it the ions in the solution which are abnormal or is it the non-ionized substance? A simple consideration would point at once to it being the non-ionized portion. We have, for example, in acetic acid a substance which behaves normally, so that the ions H^+ and Ac^- as well as the undissociated molecule HAc are normal. Similarly in ammonium hydroxide the ions NH_4^+ and OH^- as well as the non-ionized NH_3 and NH_4OH all behave normally. When we mix the two solutions there is produced a substance, ammonium acetate, which behaves abnormally. Now, on the assumption that the equilibrium we are now dealing with is

$$NH_4^+ + Ac^- \rightleftarrows NH_4Ac,$$
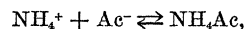
which of these molecular species is abnormal in the relation between its concentration and its activity? Probably not the ions NH_4^+ and Ac^-, because these were found to act normally in the solutions of acetic acid and ammonia. The presumption is rather that the abnormal substance is the undissociated ammonium acetate, for this occurs only in the abnormal acetate solution, and not in the normal acetic acid and ammonia. This view, that it is the non-ionized portion of the electrolyte which exhibits abnormal behavior, and not the ions, has been reached on other grounds by Noyes and others, and I hope in what follows to deduce reasons in its support.

One is apt, because the ions are in general the active constituents of an electrolyte, to lay too much stress on their behavior in considering the equilibrium in an electrolytic solution. We are justified in attributing the fact that acetic acid is a weak acid, whilst trichloracetic acid is a powerful one, rather to the properties of

the un-ionized substances than to the properties of the ions. The divergence of trichloracetic acid from the simple dilution law may similarly be due to an inherent property of the un-ionized acid, a single cause being not improbably at the bottom of both the great tendency to split into ions in water and also the abnormal behavior towards dilution.

However that may be, I think the following reasoning goes far to show that the non-ionized portion of the electrolyte is that which is primarily abnormal in its behavior, the ions acting in every way as normal. The dilution formulæ of Ostwald or of van't Hoff are essentially equilibrium formulæ. One side of the equilibrium represents the interaction of the ions to form the non-ionized substance, the other side represents the splitting up of the non-ionized substance into ions. In order to fix our ideas, we may consider a salt which obeys the empirical dilution-formula of van't Hoff. If c_u represents the molar concentration of the un-ionized portion, and c_i the molar concentration of each ion, then according to van't Hoff's empirical formula,

$$\frac{c_i^3}{c_u^2} = \text{const.}$$

If the law of mass-action were obeyed we should have, on the other hand, Ostwald's dilution formula,

$$\frac{c_i^2}{c_u} = \text{const.}$$

According to this last formula, the activity of each substance concerned varies directly as its molar concentration, and a normal result is obtained on dilution. According to van't Hoff's formula as stated above, the activity of none of the substances concerned varies directly as its concentration; but since the constancy of the expression is the only test of its accuracy, there are obviously other methods of

stating the relation which will throw the abnormal behavior either on the ions or on the non-ionized substance. Thus, if we write the equivalent form

$$\sqrt{\frac{c_i^3}{c_u^2}} = \text{const.,} \quad \text{or} \quad \frac{c_i^{1.5}}{c_u} = \text{const.,}$$

the un-ionized substance is here represented as behaving normally, and the ions abnormally; whilst if we write the formula in the form

$$\frac{c_i^2}{c_u^{1.33}} = \text{const.,}$$

the ions are represented as behaving normally, and the non-ionized substance abnormally. Now it is very important that a choice should be made amongst these three expressions, all equivalent amongst themselves so far as the mere constancy of the expression is concerned, as tested by measurements of electrolytic conductivity. Looked at from the kinetic point of view we have in the first form,

$$\frac{dx}{dt} = kc_i^3$$

$$-\frac{dx}{dt} = k'c_u^2,$$

both direct and reverse actions abnormal. In the second form, we have

$$\frac{dx}{dt} = kc_i^{1.5}$$

$$-\frac{dx}{dt} = k'c_u,$$

the ionization being normal, the recombination abnormal. And in the third form we have

$$\frac{d}{dt} = kc_i^2$$

$$-\frac{dx}{dt} \, k'c_u^{1.33},$$

the ionization being abnormal and the recombination normal.

Now, if it were possible to measure directly the velocity of either ionization or recombination, we should at once be able to select the equilibrium formula which was

really applicable. Unfortunately such velocities are so high as to be beyond our powers of measurement. Yet it seems possible to seek and obtain an answer from reaction velocities which are measurable. One assumption must be made, but it seems to me so inherently probable that few will hesitate to make it. It is this: if a substance in a given solution has normal activity with respect to one reaction, it has normal activity with respect to all reactions in which it can take part in that given solution. Similarly, if a substance in a given solution exhibits abnormal activity with respect to one reaction, it will exhibit abnormal activity with respect to all.

Granting this assumption, we have then to find a reaction in which either the ionized or un-ionized portion of an abnormal electrolyte is converted into a third substance with measurable velocity. Such a reaction exists in the transformation of ammonium cyanate into urea in aqueous and aqueous-alcoholic solutions, which was investigated some years ago by myself and my collaborators, and found to proceed at rates which could easily be followed experimentally. First of all comes the question: Is the urea formed directly from the ions or from the un-ionized cyanate? As Wegscheider pointed out, it is impossible from reaction-velocity alone to determine which portion passes directly into urea, if the velocities of ionization and recombination are infinitely greater than that of the urea-formation, as is undoubtedly the case. Other circumstances make it highly probable that the ions are the active participants in the transformation, but we may leave the question open, and discuss the results on both assumptions.

Suppose, first, that the un-ionized cyanate is transformed directly into urea. Then we have the successive reactions

$$NH_4^{\cdot} + CNO' \rightleftarrows NH_4CNO \rightarrow CO(NH_2)_2.$$

The slight reverse transformation of urea into cyanate may for the present purpose be neglected, as it in no way influences the reasoning to be employed.

If the un-ionized substance behaves normally, then the conversion of the ammonium cyanate into urea, when referred to the un-ionized substance, will appear unimolecular and obey the law of mass-action: when referred to the ionized substance it will not appear to be bimolecular and will not obey the law of mass-action.

Suppose, now, that the direct formation of the urea is from the ions. Then we are dealing with the actions

$$NH_4CNO \rightleftarrows NH_4^{\cdot} + CNO' \rightarrow CO(NH_2)_2.$$
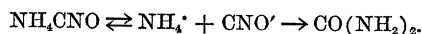
Again, let us assume the un-ionized substance to be normal. Once more, if the transformation is referred to the non-ionized substance it will appear as monomolecular; when referred to the ionized substance it will not appear as bimolecular, as it should if the mass-action law were obeyed.

It is a matter of indifference, then, so far as the point with which we are dealing is concerned, whether the ionized or the non-ionized cyanate is transformed directly into urea. If the non-ionized cyanate behaves normally the action when referred to it will in either case appear to be strictly monomolecular.

If the ionized cyanate, on the other hand, behaves normally, the reaction when referred to it will be bimolecular and normal; when referred to the non-ionized cyanate it will not be monomolecular, and therefore will be abnormal.

The actual experiments show that whether water or a mixture of water and alcohol be taken as solvent, the reaction when referred to the ions is strictly bimolecular; when referred to the non-ionized substance it is not monomolecular, *i. e.,*

proportional to c_u, but rather proportional to a power of c_u other than the first, namely, $c_u^{-1.4}$.

This is, to my mind, a very strong piece of evidence that in the case of the abnormal electrolyte, ammonium cyanate, the abnormality of the ionization equilibrium is to be attributed entirely to the non-ionized portion. But ammonium cyanate differs in no respect, with regard to its electrolytic conductivity, from the hundreds of other abnormal binary electrolytes with univalent ions; and I am therefore disposed to conclude that it is to the non-ionized portion in general of these electrolytes that the abnormality is to be attributed.

As I have already indicated, this conclusion is not altogether novel, but in my opinion it has not been sufficiently emphasized. Even in discussions where it is formally admitted that the divergence from the dilution law may be due to the non-ionized portion, yet the argument is almost invariably conducted so as to throw the whole responsibility on the ions. The point which ought to be made clear is whether the constant k of the equation

$$\frac{dx}{dt} = kc_i{}^2,$$

or the constant k' of the reverse equation

$$-\frac{dx}{dt} = k'c_u,$$

is really constant. If the former, then the ions are truly normal, and primary explanations of the abnormality of the strong electrolytes can scarcely be sought in high total ionic concentrations and the like, though a connection between the two no doubt exists, both being determined by the same cause.

In my illustration I have assumed that there holds good a dilution law of the kind given by Storch, of which van't Hoff's dilution law is a particular case. Here the active mass is represented as a power of the concentration other than the first power. The argument I have used is altogether independent of this special assumption; the active mass of the abnormal substance may be any function of its concentration, and the same conclusion will be reached.

Nernst's principle of the constant ionic solubility product affords additional evidence that the ions act normally in solution. In deducing this principle it is generally assumed that it is the constant solubility of the non-ionized salt that determines the final equilibrium. This assumption, though convenient, is not necessary. The equilibrium is a closed one, thus:

Ions / Solid Salt ⇆ Non-ionized Salt
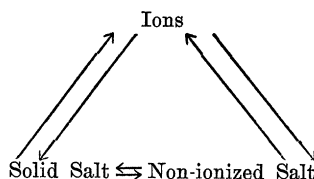
The solid is not only in equilibrium with the non-ionized salt but also with the ions. Now, in the deduction of the change of solubility caused by the addition of a substance having one ion in common with the original electrolyte the mass-action law for ionization is assumed. This is of course justified when we deal with feeble electrolytes, but in the case of salts and strong acids which do not follow the mass-action law the experiments are found still to be in harmony with the theoretical deductions. This is not only so when the two substances in solution are both abnormal, but also when one is abnormal and the other normal, no matter which is used to produce the saturated solution. In fact, the principle of the constant ionic solubility product may be employed with equal success to calculate the effect on the solubility of one electrolyte of the addition of another electrolyte with a common ion, whether both electrolytes are normal, both abnormal, or whether one is normal and the other abnormal. At

first sight, this apparent obedience of abnormal electrolytes to the mass-action law seems strange, but a little consideration shows that if it is only the non-ionized portion of a salt that is truly abnormal, the theoretical result is to be expected. Suppose that the ions do behave normally in the ionization, then they must also act with normal active mass with reference to the solid, with which they may be regarded as in direct equilibrium according to the closed scheme referred to above. A change, then, in the concentration of any one of the ions, brought about by the addition of a foreign salt with that ion, will necessarily bring about the change in solubility of the salt calculated from the mass-action law, so far at least as experiment can tell us, for any variation from theory is caused by the change in the nature of the solvent due to the addition of the foreign substance. We ought, then, on the assumption that the ions behave normally, to expect that the principle of the constant solubility product would yield results of the same degree of accuracy in dilute solutions whether the electrolytes considered were normal or abnormal. This, as I have said, is actually the case.

To put the whole matter briefly, in the equilibrium between electrolytes agreement will be obtained between theory and experiment whether we use the mass-action law, or an empirical law such as van't Hoff's dilution formula, provided only that we attribute the abnormality to the non-ionized portion of the electrolyte. Thus we can deduce the ordinary formulæ for hydrolysis or for isohydric solutions as readily for abnormal as for normal electrolytes, and find the most satisfactory agreement with experiment in both cases.

By this one simple assumption, then, for which I have offered some direct justification, it is possible to find a basis for calculation with abnormal electrolytes. The problem of *why* certain electrolytes should be normal and others abnormal is, of course, in no way touched by this assumption. That is a matter for further investigation and research.

Another great desideratum of the theory of solutions is to find a general basis for the calculation of hydrates. The present position of the theory of hydrates in solution may perhaps most aptly be compared to the theory of electrolytic dissociation for solvents other than water. That hydrates exist in some aqueous solutions is undoubted, but no general rule or method exists for determining what the hydrates are and in what proportions they exist. Similarly the theory of electrolytic dissociation applied to other than aqueous solutions affords no general means of determining what the ions are and how great is the degree of ionization. It is only for aqueous solutions that Arrhenius was able to give a practically realizable definition of degree of ionization, and it is on this definition that the whole effective work on aqueous electrolytes is based; and until some general practically applicable principle of a similar character is attained for hydrates, the work done on that subject, however interesting and important it may be in itself, must necessarily be of an isolated character.

Arrhenius did not originate the doctrine of electrolytic dissociation or free ions: that was enunciated in 1857 by Clausius, and remained relatively barren. What he did was to introduce measurable quantities into the doctrine, and to show its simple quantitative applicability to aqueous solutions; immediately it became fertile. And as soon as a simple quantitative principle is developed for hydrates in solution, that doctrine will become fertile also.

It is surely now time that all the irrelevant and intemperate things that have

been said and written by supporters of the osmotic pressure and electrolytic dissociation theories on the one hand, and by those of the hydrate theory on the other, should be forgotten. Far from being irreconcilable, the theories are complementary, and workers may, each according to his proclivity, pursue a useful course in following either. One type of mind finds satisfaction in using a handy tool to obtain practical results; another delights only in probing the ultimate nature of the material with which he works. For the progress of science both types are necessary—the man who determines exact atomic weights as well as the man who speculates upon the nature of the atoms. That the want of knowledge as to what the exact nature and mechanism of osmotic pressure is, should prevent accurate experimental work being done on it, or interfere with its use in theoretical reasoning, is equally ridiculous with the proposition that because in the theory of osmotic pressure we have a good quantitative tool for the investigation of solutions, therefore we should abandon altogether the problem of its nature.

The fundamental ideas of a science are the gift to that science of the few great masters; the many journeymen investigators may be trusted to utilize them according to their abilities. Having once given his great principles to the world, van't Hoff remained practically a spectator of their development; but by his single act he provided generations of chemists with useful and profitable fields for their labor.

<div style="text-align: right">J. WALKER</div>

THE COAL PRODUCTION OF PENNSYLVANIA

PENNSYLVANIA's coal production in 1910 was 235,006,762 short tons, valued at $313,304,812. Of this 84,485,236 short tons was anthracite, valued at $160,275,302, and 150,521,526 short tons was bituminous coal, valued at $153,-

029,510. Compared with 1909, when the total production of the state amounted to 219,037,-150 short tons, valued at $279,266,824, the production in 1910 shows an increase of 15,969,612 short tons, or 7 per cent., in quantity, and of $34,037,988, or 12.2 per cent. in value. Of the total increase 3,314,877 short tons was in the production of anthracite and 12,554,735 short tons in the production of bituminous coal. The value of the anthracite production showed an increase of $11,-093,713, or 7.4 per cent., and that of bituminous coal increased $22,944,273, or 17.64 per cent. Although the quantity of bituminous coal produced exceeded that of anthracite by nearly 80 per cent., the value of the anthracite product was larger than that of the bituminous output by nearly $7,250,000. Bituminous coal represented 63.6 per cent. of the total output and anthracite represented 51 per cent. of the total value.

The anthracite mines of Pennsylvania gave employment to 169,497 men, who worked an average of 229 days. The bituminous mines employed 175,403 men for an average of 238 days. The average production for each man employed in the anthracite region was 498 short tons during the year. In the bituminous mines the men averaged 825 tons each. The daily average production for each employee in the anthracite region was 2.17 short tons and in the bituminous districts it was 3.61 tons. According to the Pennsylvania Department of Mines 601 men were killed and 1,050 were injured in the anthracite mines in 1910. The fatal accidents in the bituminous mines numbered 539 and the nonfatal accidents numbered 1,142.

In the combined production of anthracite and bituminous coal Pennsylvania outranks any of the coal-producing countries of the world except Great Britain and Germany, and in 1910 it came within 10,000,000 short tons, or less than 5 per cent., of equalling the output of Germany. Pennsylvania's production in 1910 was more than four times that of Austria-Hungary in 1909, and more than five times that of France in 1910, and nearly 20 per cent. of the total coal production of the